

March 6, 2005

DECLARATION

The undersigned, Dana Scruggs, having an office at 8902B Otis Avenue, Suite 204B, Indianapolis, Indiana 46216, hereby states that she is well acquainted with both the English and German languages and that the attached is a true translation to the best of her knowledge and ability of PCT/DE 03/03069 (INV.: MUEHLIG, C., ET AL), entitled "Determining the Suitability of an Optical Material for the Production of Optical Elements, Corresponding Device, and Use of Said Material".

The undersigned further declares that the above statement is true; and further, that this statement was made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or document or any patent resulting therefrom.



Dana Scruggs

DETERMINING THE SUITABILITY OF AN OPTICAL MATERIAL FOR THE
PRODUCTION OF OPTICAL ELEMENTS, CORRESPONDING DEVICE, AND
USE OF SAID MATERIAL

Description

The present invention related to a method for determining the suitability of an optical material for the production of optical elements, a device for carrying out the method, and the use of the optical materials determined using the method.

It is known that materials used to produce optical elements absorb irradiating light to a greater or lesser extent, so that the intensity of the light and/or radiation is typically less after it passes through an optical element than before it passes through. It is also known that the extent of this absorption depends on the wavelength of the light. For optical systems, i.e., for optically transparent systems, the goal, however, is to keep the absorption as low as possible, i.e., they should have a high light permeability or transmission, at least for the particular working wavelength. The absorption is composed of material-specific (intrinsic) portions and portions due to "non-intrinsic" portions, such as inclusions, contamination and/or crystal imperfections. While the intrinsic absorption is independent of the particular quality of the material, the additional radiation absorption of the non-intrinsic absorption results in a degradation of the optical material.

As a result of the intrinsic and non-intrinsic absorption, energy is deposited in the optical material, which results in a temperature rise. The disadvantage of the material heating in this manner is that the optical properties, e.g., the refractive index, change, which results in a change in the reproduction ratios in an optical component used for beam shaping, for example, since the refractive index depends not only on the wavelength of the light, but also on the temperature of the optical material. In addition, a temperature rise in an optical component also

1 results in a change in the lens geometry. These phenomena produce a change in
2 the lens focal point and blurriness in images projected with the heated lens. In
3 photolithography in particular, which is used to produce computer chips and
4 electronic circuits, this results in quality degradations and/or an increase in
5 waste, and is therefore not desired.

6
7 With many materials, a portion of the absorbed radiation is not only converted to
8 heat, but is also given off again in the form of fluorescence. The formation of
9 fluorescence on optical materials, in particular on optical crystals, is known per
10 se. For example, W. Triebel et al. describe, in Proceedings SPIE Vol. 4103,
11 pages 1 - 11, 2000 Triebel, Bark-Zollmann, Mühlig et al. in "Evaluation of Fused
12 Silica for DUV Laser Applications by Short Time Diagnostics", the formation and
13 measurement of laser-induced fluorescence (LIF) in quartz, particularly in OH-
14 rich quartz and/or a glass matrix. Furthermore, M. Mizuguchi et al. describe, in J.
15 Vac. Sci. Technol. A., Vol. 16, pages 2052 – 3057 (1998), the formation of optical
16 absorption bands in a calcium fluoride crystal. In addition, M. Mizuguchi et al.
17 describe, in J. Opt. Soc. Am. B, Vol. 16, pages 1153 – 1159, July 1999, a time-
18 resolved photoluminescence for diagnosing the laser damage done to a calcium
19 fluoride crystal. This article describes the formation of color centers that form
20 photoluminescence via excitation with an ArF excimer laser at 193 nm. To enable
21 measurements of this type, however, crystals with a relatively high amount of
22 impurities are used in this case, and this does not fulfill the high requirements for
23 photolithography. In addition, the fluorescence measurement is carried out in the
24 sample to be investigated after a waiting period of 50 nsec after the laser pulse
25 ends. It has been shown that the fluorescence values obtained in this manner
26 cannot be used for quality control purposes or to determine the extent of the
27 impurity, and therefore cannot be used to form color centers in the high-quality
28 crystals.

29
30 It is therefore believed that the determination of radiation-induced fluorescence,
31 in particular laser-induced fluorescence, cannot be used for quality control of

1 high-quality, optical materials, as with high-purity calcium fluoride for
2 photolithography, for example. (Refer also to the presentation by Dr. Mann,
3 Laserlabor Göttingen, SPIE Conference in Seattle, USA, July 2002). It was
4 determined that a correlation cannot be made between laser-induced
5 fluorescence and a claim regarding impurities and the optical quality of a
6 material.

7
8 The object of the present invention, therefore, is to provide a test with which an
9 optical material can be tested for its suitability for use as an optical element and,
10 in fact, tested in general for use at certain working wavelengths. The test should
11 be easy to perform and require very little equipment. Finally, it should be possible
12 to carry out the test with as little background as possible, i.e., the results should
13 contain no background effects, if possible, and it should be possible to carry out
14 the test with very high sensitivity. In addition, it should be possible to also
15 determine, in the most selective manner possible, interference by impurities in
16 high quality crystals that are present in small amounts and are impossible or very
17 difficult to detect, and to assign them to the particular contaminating substance.

18
19 In addition, it should be possible, using the method, to determine the amount and
20 type of impurity in the particular sample, regardless of the sample size, and
21 without extensive calibration.

22
23 All of these objectives are attained by the method and device defined in the
24 claims.

25
26 According to the present invention, it was found that the problems of the related
27 art cited above can be prevented by determining the non-intrinsic fluorescence
28 during excitation with light and/or immediately after a light pulse ends, i.e., after
29 the light pulse has passed through the sample. It has been shown that, with
30 measurements carried out according to the related art, the non-intrinsic
31 fluorescences have already decayed greatly due to their short lives, which are in

1 the nanosecond range. For this reason, these measurements contain only very
2 slight non-intrinsic fluorescence signals.

3
4 This is avoided with the method according to the present invention and by
5 optimizing the non-intrinsic fluorescence signals. The radiation-induced
6 absorption and, in particular, the absorption induced by flaws and/or impurities
7 can be easily characterized in this manner.

8
9 In a preferred embodiment according to the present invention, the intrinsic
10 fluorescence is determined in addition to the non-intrinsic fluorescence, for
11 standardization purposes. Since, in fact, the intrinsic fluorescence is a material
12 constant, the size ratio of non-intrinsic to intrinsic fluorescence can be used to
13 standardize the non-intrinsic bands and thereby quickly determine whether the
14 optical material being tested is suitable for further processing to an optical
15 element such as a lens, prism, etc. In addition, this ratio can be used—with
16 reference to a simple calibration curve—to determine the amount of a particular
17 impurity at any time without the need to perform elaborate calibrations, e.g.,
18 dimension determinations, etc., on the sample to be investigated.

19
20 Non-intrinsic fluorescence bands are preferably used to carry out the method
21 according to the present invention. Preferred non-intrinsic bands are those at
22 wavelengths 313 nm, 333 nm, 365 nm, 420 nm, 450 nm, 500 nm, 580 nm, 740
23 nm and 225 nm. It was found that the fluorescence wavelength 225 nm is
24 produced only at irradiation with a wavelength of 157 nm (F_2 laser), although this
25 does not exist in every material. Highly preferred, however, is the determination
26 of fluorescence at the wavelength 580 and/or 740 nm. These fluorescence bands
27 are typically found and have proven to be particularly sensitive in the method
28 according to the present invention. The fluorescence at 450 nm is also
29 particularly crucial. This band is not as sensitive to the fluorescence and/or
30 irradiated energy density, although it has a noticeably strong influence on the
31 initial transmission T_0 . According to the present invention, when an intrinsic

fluorescence band occurs, it is used to standardize the non-intrinsic fluorescence. The intrinsic fluorescence band at 278 nm is preferably used for standardization. It has been shown that this band is free of other non-intrinsic components. For this reason, it is particularly well-suited for standardization. The standardization of the level of the measured, non-intrinsic fluorescence band or bands is carried out by calculating the ratio of non-intrinsic to intrinsic fluorescence. Of particular preference in the method according to the present invention, the non-intrinsic fluorescence is determined synchronously with the irradiated laser pulse.

It has proven particularly advantageous to treat the material to be determined with pre-irradiation before carrying out the method according to the invention. In this procedure, a predetermined number of laser pulses is used to determine the absorption state of the material with regard for "rapid damage" and/or "rapid annealing", so that each of the subsequent measurements is carried out from one even base level. Typical pulse amounts for ArF lasers (193 nm) are at least 3000, preferably at least 6000, and, with an irradiation wavelength of 157 nm (F₂ laser), they are 30,000, and preferably 70,000 – 200,000 laser pulses. In principle, to carry out the method according to the present invention, it is necessary to irradiate the material to be investigated with the most comparable energy densities possible. The method is also preferably carried out not only with the same or a comparable energy density, but also preferably at the same excitation and fluorescence wavelengths to obtain comparable values and spectra, in particular.

With the method according to the present invention it is also possible to test the suitability of an optical material for any excitation wavelength and, in fact, before any type of further processing to form an optical element or component. It is possible, for example, to determine the exact intrinsic fluorescence at an excitation wavelength of 193 nm and 157 nm and to take it into account in the determination of the non-intrinsic fluorescence and to thereby classify the optical

1 material as suitable for one or the other wavelength, depending on the
2 application.

3
4 Finally, the type of impurities can also be easily determined, even in amounts in
5 the ppb range, from the fluorescence spectrum. Based on the ratio of intrinsic to
6 non-intrinsic fluorescence, it is also possible to determine the amount of impurity
7 that is producing the fluorescence. Typical contaminating materials are rare
8 earths and, in particular, Cer, europium, terbium, sodium and oxidic oxygen.

9
10 According to the present invention, the determination method is preferably
11 carried out with UV light and, in particular, deep UV light. Wavelengths below 250
12 nm, in particular below 200 nm, have proven advantageous, and wavelengths
13 between 100 and 150 nm and 200 nm are particularly preferred. Advantageously,
14 the method is carried out at the excitation wavelength with which the optical
15 material will be irradiated during subsequent use. A preferred radiation source for
16 the high-energy light is a laser, whereby laser pulses with working wavelengths
17 of 193 and/or 157 nm are preferred.

18
19 In the method according to the present invention, the non-intrinsic fluorescence is
20 preferably measured with a grating spectrograph and an I-CCD camera
21 (intensified charged coupled device) with adjustable illumination intervals,
22 whereby it is preferable to use a computer to process the spectrum obtained.
23 Measurements and devices of this type are known to one skilled in the art, and
24 are described, for example, by W. Triebel et al. in Proceedings SPIE Vol. 4103,
25 pages 1 through 11, 2000, "Evaluation of Fused Silica for DUV Laser
26 Applications by Short Time Diagnostics", and by Mizuguchi et al. in J. Opt. Soc.
27 Am. B, Vol. 16, 1153 ff. (July 1999).

28
29 It is particularly preferred according to the present invention to locate a barrier
30 device between the fluorescent sample to be investigated and the fluorescence
31 measurement device, the barrier device preventing passage by the typically high-

1 energy excitation radiation. Barrier devices of this type that hide any excitation
2 wavelengths are known to one skilled in the art. The hiding can take place in any
3 manner. One possibility is for these wavelengths to be hidden using a grating
4 spectrograph located in front of the CCD camera that divides the absorbed light
5 into its various wavelengths. By locating and/or rotating the spectrograph
6 accordingly, it is possible to block or deflect the excitation wavelength separated
7 out of a high-energy radiation source. It is also possible, in principle, to rotate the
8 grating spectrographs of the CCD camera itself.

9
10 A further possibility is to use wavelength-specific filters, such as dielectric thin-
11 layer filters, which can also be produced in a selective manner today for any
12 wavelength. Filters of this type are typically produced by applying a
13 corresponding multilayer reflective layer on a carrier material that prevents
14 passage by the undesired wavelengths.

15
16 Layer filters of this type are preferred in the method according to the present
17 invention. It is also necessary, however, that the filters used not have any
18 intrinsic fluorescence produced by the incident light, so that the measured results
19 are not adulterated.

20
21 With the method according to the present invention, it is also now possible to
22 determine fluorescences, the wavelengths of which are close to the excitation
23 wavelength. This is particularly significant for the use of optical elements in
24 photolithography, since the energy of fluorescence wavelengths of this type is
25 also sufficient to expose the photosensitive resist of a waver, which results in a
26 strong loss of contrast in the circuit pattern projected onto the wafer.

27
28 The determination of the fluorescence according to the present invention
29 preferably takes place within or immediately after an exposure interval on the
30 material. It takes place preferably within a time segment after the material
31 exposure has ended, the time segment corresponding to the particular

characteristic decay curves and/or lives of the various non-intrinsic fluorescences, and/or is adapted thereto. In a large number of cases, 90%, in particular 80% and often 70% of the decay time has proven advantageous for the measurement. In a few preferred optical materials, the method according to the present invention and/or the determination is carried out within a time period and/or time segment of less than 50 nsec after the irradiation and/or the irradiation pulse in the material ends, whereby the determinations of up to max. 40 and preferably up to max. 30 nsec are particularly preferred. In a few cases, measurements within a time of less than 15 nsec have even proved advantageous, after the radiation pulse has passed through the material.

Of the CCD cameras used in the method according to the present invention, "OMAs" (optical multichannel analyzers) are preferred, particularly when they have adjustable exposure and/or measurement intervals. A camera of this type has a detection limit of less than 10 photons and therefore enables short exposure times, e.g., of 10 nsec or even as short as 150 psec. Cameras of this type are commercially available from Roper Scientific, USA, for example.

The method according to the present invention is suitable for use with any optical materials that develop a fluorescence when irradiated, whereby crystalline, optical materials are preferred, in particular halogenidic and/or fluoridic monocrystals. Particularly preferred are alkaline and/or earth alkaline fluorides, whereby calcium fluoride, barium fluoride, strontium fluoride, lithium fluoride, potassium fluoride, sodium fluoride and/or magnesium fluoride and a mixture, such as KMgF_3 are very preferably preferred.

The present invention also relates to a device for carrying out a particularly preferred method according to the present invention. A device of this type includes a radiation source for transmitting an excitation wavelength, a sample holder for holding a material sample to be determined, and a device for determining a fluorescence induced in the material sample by excitation

wavelength. The excitation wavelength travels along a typically linear beam path that starts at the radiation source, through the material sample, and preferably enters a reference photodiode. According to the present invention, the fluorescence determination device is located outside this beam path, so that no excitation wavelength can strike the fluorescence determination device directly. The device is preferably arranged such that the fluorescence to be measured describes a fluorescence beam path that extends perpendicularly to the excitation beam path. The fluorescence measurement device typically includes one or more optical lenses that bundle the fluorescence emitted by the material sample to be investigated in a polychromator and/or a grating spectrograph. The fluorescent light that is broken down into its individual wavelengths in the spectrograph is then deflected to a CCD camera, in particular an I-CCD, in which the intensity of the individual wavelengths is determined and is preferably processes and stored using a computer and/or a data processing system. The fluorescence points determined and stored in this manner using the CCD camera can now be easily compared with stored standard values and determined in the computer.

The device according to the present invention is unique in that a barrier element is located between the material sample to be tested and the CCD camera that prevents the high-energy excitation wavelength from passing through to the CCD camera. By way of the barrier element located in the device according to the present invention, it is ensured that no light from the radiation source reaches the CCD camera. This barrier element also prevents scattered light from the excitation wavelength from reaching the CCD camera, which could not only falsify the measurement but also destroy this highly sensitive camera. The barrier element used according to the present invention should not fluoresce itself at the excitation wavelengths and thereby falsify measured fluorescent values.

All types of devices that deflect, reflect or absorb a certain wavelength are suitable for use as the barrier element. The simplest configuration is an optical

1 grating, for example, as included in a polychromator and/or spectrographs. In a
2 further preferred exemplary embodiment according to the present invention, the
3 barrier element includes a wavelength-specific filter, in particular a multilayer
4 filter, in the case of which a double layer or multiple reflective layers are applied
5 that blank out or reflect the particular wavelength. A particularly preferred filter is
6 a dielectric thin-layer filter.

7
8 It has been shown that it is possible with filters of this type to also determine
9 fluorescences that are close to the excitation wavelength. Fluorescences of this
10 type are fatal with photolithography in particular, since they can expose a
11 photosensitive resist due to their vicinity to the excitation wavelength, just like the
12 excitation wavelength itself, and therefore noticeably reduce the sharpness
13 and/or contrast of a projected circuit pattern.

14
15 With the method according to the present invention it is therefore possible in the
16 production of optical devices to not only exclude, at an early stage, optical
17 materials from further processing that have high non-intrinsic fluorescence but
18 also those that have a fluorescence close to the excitation wavelength.

19
20 The optical materials determined according to the present invention are
21 particularly suited to the production of optical components in DUV lithography,
22 and to the production of wafers coated with photosensitive resist and, therefore
23 to the production of electronic devices. The present invention therefore also
24 relates to the use of materials obtained using the method according to the
25 present invention and/or in the device according to the present invention in the
26 production of lenses, prisms, light-conducting rods, optical windows and optical
27 devices for DUV lithography, in particular in the production of steppers and
28 excimer lasers and, therefore, to the production of integrated circuits, computer
29 chips and electronic devices such as computers and other devices that contain
30 chip-like integrated circuits.

31